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Reaction of Boron Trichloride with Methoxyamine Hydrochloride

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REACTION OF BORON TRICHLORIDE WITH METHOXYAMINE HYDROCHLORIDE

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ABSTRACT

Boron trichloride and methoxyamine hydrochloride were reacted in refluxing chlorobenzene and again in a refluxing mixture of chlorobenzene and chloroform. Procedures for handling and analyzing samples under anhydrous conditions are discussed. Evidence is given for the formation of B-trichloro-N-trimethoxyborazine in the chlorobenzene/chloroform system.

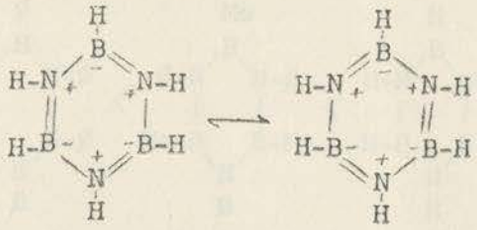


Figure 1, Kékulé structures for borazine

Laubengayer. Ryschkewitz, et al, used methylammonium chloride instead of ammonium chloride and also used an excess of boron trichloride.

The use of Grignard reagents on B-trichloro-N-trialkylborazines allows the preparation of borazines with aliphatic or aromatic groups attached to all six sites on the ring. The thermal stability of a group of such compounds was studied by Newsom, et al,[4] and is summarized in figure 2. Among the compounds studied, Newsom, et al, found the greater stability in compounds with electron donating groups at all sites on the ring. In compounds with electron withdrawing groups present, greater stability was found in the structure with such groups located on nitrogen. This illustration of stability suggests that B-trichloroborazine would be less stable than hexaalkylborazines because of the electron withdrawing nature of chlorine. This electron withdrawing effect may be, in part, cancelled by a mesomeric effect of electrons in p orbitals in chlorine, reducing the amount of stability lost due the presence of chlorine.

Konig[5], in 1966, reacted boron trichloride with methoxyamine hydrochloride in refluxing chlorobenzene and presented evidence for the formation of B-trichloro-N-trimethoxyborazine. The reaction is essentially the same as that used by Ryschkewitz, et al, to prepare the N-methyl compound, the difference being the use of methoxy- rather

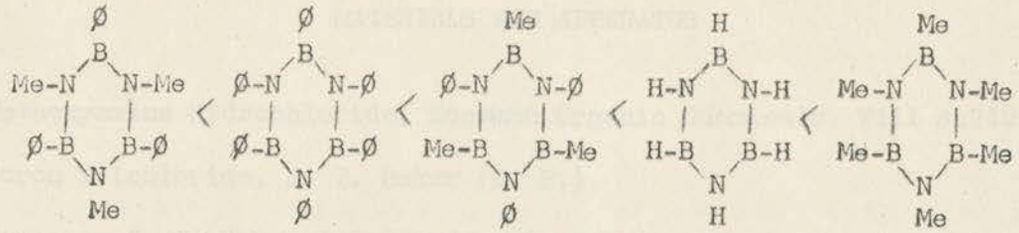


Figure 2, thermal stability

than methyl-ammonium chloride. Stability of B-trichloro-N-trimethoxy-borazine should be at least comparable to that of B-trichloroborazine or B-trichloro-N-trimethylborazine due to the addition of an electron donating group to the nitrogen sites in the ring.

The current work consists of several attempts to obtain better yields and purities of B-trichloro-N-trimethoxyborazine through use of reaction conditions similar to those used by Konig.

The first reaction attempted involved the use of triethylamine to consume the hydrochloric acid produced. Removal of one of the products was expected to result in a larger yield of the borazine.

For the second and third reactions a mixture of chlorobenzene and chloroform was used to obtain a lower reflux temperature. The lower temperature was used when analysis of previous products suggested the formation of the adduct of boron trichloride and methoxyamine rather than the borazine. A mixture of 95 ml of chlorobenzene and 22 ml of chloroform was found to boil at 107-8°C in the reaction apparatus used. As fractionation must occur in such a system, it is doubtful that the same mixture would boil at the same temperature if a different size flask or condenser was used.

MATERIALS AND APPARATUS

Methoxyamine Hydrochloride, Eastman Organic Chemicals, Will #4712

Boron Trichloride, J. T. Baker (C. P.),

Benzene, J. T. Baker (purified, anhydrous)

Chlorobenzene, J. T. Baker (reagent), Will # B-9179

Triethylamine, Eastman Organic Chemicals,

Chloroform, J. T. Baker (reagent), Will # B-9183

Nitrogen, Airco (oxygen pumped)

Glove Box, Forma Scientific, Inc.

IR spectrophotometer, Perkin-Elmer #621

EXPERIMENTAL

Preparation of Solvents and Reagents.

All solvents used were kept as dry as possible. Chlorobenzene, benzene, and triethylamine were stored over clean sodium metal to minimize water content. All liquids were measured with dry graduated cylinders and transferred from storage bottle to reaction flask as quickly as possible.

Methoxyamine hydrochloride was stored in a dry glove box. Weighing of $MeONH_3Cl$ was done in a closed weighing bottle to prevent water contamination. The $MeONH_3Cl$ was added or removed from the weighing bottle in the glove box and the bottle taken out of the glove box for weighing. After the reaction system had been dried and a flow of dry nitrogen established, the weighing bottle was opened in the stream of nitrogen escaping from one of the necks of the reaction flask and the $MeONH_3Cl$ poured in.

Nitrogen was dried through a phosphorous pentachloride/glass beads drying tube. Excess pressure to the drying tube was prevented by a mercury bubbler. Nitrogen escaping through the bubbler to the atmosphere was also passed through a tube of sulfur to trap mercury vapors.

Boron trichloride was stored in the metal cylinder in which it was purchased. This cylinder was fitted with a length of polyethlene tubing and a standard taper ground glass joint. Figure 3 shows the original arrangement in which the graduated tube, stopcock #3, and ground glass joint were transferred from the vacuum line to the reaction line between distillation and use of the BCl_3. Figure 4 shows a more

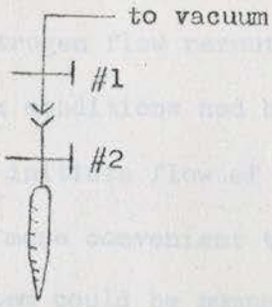


Fig 3

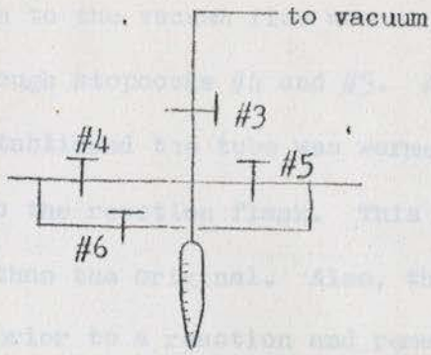


Fig. 4

recent system in which the vacuum line and the reaction line were connected with a length of polyethylene tubing.

In the first system the transfer assembly and the BCl_3 cylinder were connected to a vacuum line, the graduated tube cooled in dry ice/acetone, and the BCl_3 vacuum distilled until an excess of the liquid was in the graduated tube. The tube was then warmed to 0°C in ice water and the BCl_3 pumped off until the desired volume (±0.1 ml) remained in the graduated tube. Stopcocks #1 and #2 were then closed, and the transfer assembly moved from the vacuum line to the reaction line. When the transfer assembly had been connected to the nitrogen line leading to the reaction flask, and reflux conditions established, the tube containing the BCl_3 was allowed to warm to 12-14°C and stopcock #2 opened to allow BCl_3 to be carried into the reaction flask by the nitrogen stream.

In the second system BCl_3 was vacuum distilled into the graduated tube while the nitrogen flow was shunted through stopcock #6 to maintain dry conditions in the reaction flask. When the desired volume of BCl_3

was in the graduated tube, the line to the vacuum line was shut off and the nitrogen flow rerouted through stopcocks #4 and #5. Again, when reflux conditions had been established the tube was warmed to 12-14°C to initiate flow of BCl_3 to the reaction flask. This second system was more convenient to use than the original. Also, the second system could be pumped dry prior to a reaction and remain sealed against moisture in the air until the end of the reaction.

Reaction Apparatus.

The system used for the first reaction (fig. 5) consisted of a two neck, one liter flask fitted with a heating mantle, stirrer, condenser, and gas induction system. The tip of the gas inlet was below the surface of the liquid in the reaction flask and just cleared of the stirrer blade. A safety flask was connected to the system to prevent damage to the rest of the system due to any pressure build up. The connection of the safety flask was not rigid and would open in any appreciable pressure built up within the system. A calcium chloride drying tube was mounted at the top of the water cooled condenser to further protect the system from water contamination. The stirring assembly consisted of a ground glass rod and bushing fitted to the reaction flask. A teflon blade was used, and speed was controlled with an autotransformer.

The reaction system used for the second and third reactions (fig. 6) incorporated several improvements over the original apparatus. In the newer system the gas inlet extended under the stirring blade

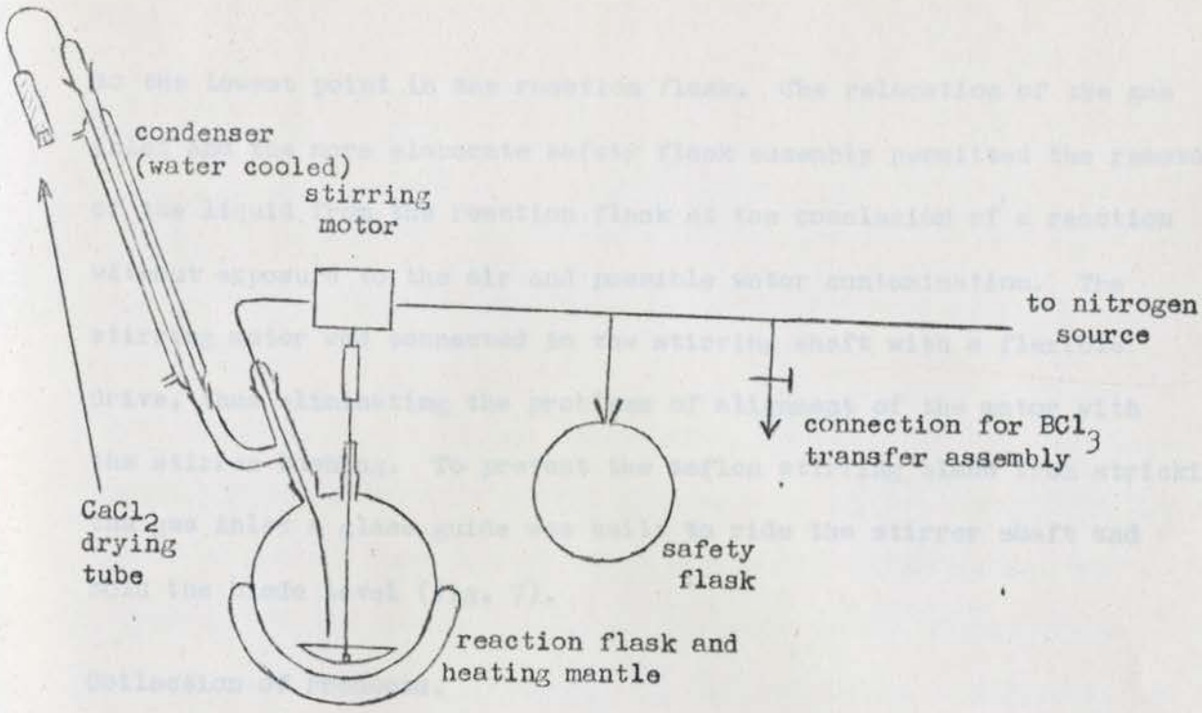

condenser
(water cooled)
stirring
motor
to nitrogen
source
connection for BCl_3
transfer assembly
$CaCl_2$
drying
tube
safety
flask
reaction flask and
heating mantle

Fig. 5

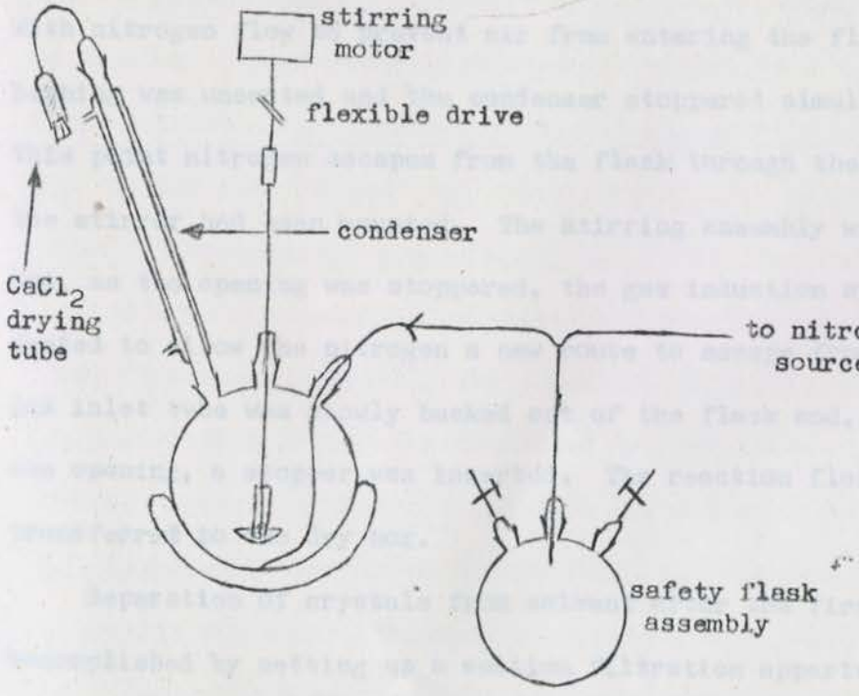

stirring
motor
flexible drive
condenser
$CaCl_2$
drying
tube
to nitrogen
source
safety flask
assembly

Fig. 6

Fig. 7

dry box (fig. 8). A rotary vacuum pump, protected by a dry ice/acetone trap, was connected to a needle valve mounted on the side of the dry box. A 250 ml filtration flask, with a 125 ml safety flask, was connected to the inside fitting of the above needle valve. To a second needle valve was attached a P_2O_5/glass beads drying tube. As air inside the dry box was lost to the pump during filtration dry air entered through the drying tube.

As a means of warming the solution, a one liter heating mantle was taken into the dry box and connected to an autotransformer outside of the box. Since heating an organic solvent in a confined space could produce an explosion hazard, all electrical contacts inside of the dry box were cleaned and taped before use. No switches or other sources of electrical sparks were used in the dry box.

After the solvent and crystals had been warmed to about 70°C, filtration was attempted. The formation of a gelatinous material on the filter soon slowed the flow rate to near zero. Eventually a mass of dry, crystaline material (product I), was obtained. An infrared spectrum was obtained from this solid. The filtrate from the above filtration was pumped to dryness at room temperature. The solid that was thus obtained was tar-like in nature and no analysis was attempted.

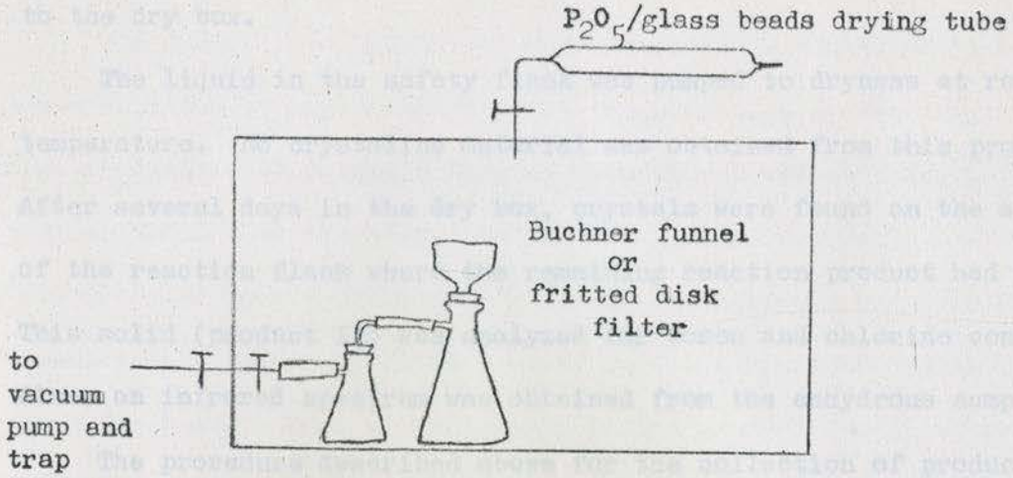


Fig. 8

Due to the low yield of solid on the filter, no further work-up was attempted.

After the second reaction (in chlorobenzene/chloroform solvent) the bulk of liquid and solid content of the reaction flask was pumped into the safety flask by connecting a vacuum pump to one of the extra fittings on the safety flask, shutting off the nitrogen flow, and (carefully) opening the stopcock in the safety flask fitting. As soon as the transfer was complete the stopcock controlling flow to the vacuum pump was closed and the line to the vacuum pump replaced with a line to the dry nitrogen supply. Both stopcocks on the safety flask assembly were then opened to establish a flow of dry nitrogen. As the safety flask was disconnected from the reaction line, the stopcock controlling nitrogen flow out of the safety flask was closed. When the center neck of the flask was stoppered, the remaining stopcock was closed, the nitrogen supply line removed, and the flask transferred

to the dry box. As before, the reaction flask was sealed and removed to the dry box.

The liquid in the safety flask was pumped to dryness at room temperature. No crystaline material was obtained from this procedure. After several days in the dry box, crystals were found on the sides of the reaction flask where the remaining reaction product had dried. This solid (product II) was analyzed for boron and chlorine content. Also, an infrared spectrum was obtained from the anhydrous sample.

The procedure described above for the collection of products was repeated, with one modification, after the third reaction. In this collection, the flow of solvent from reaction flask to safety flask was maintained at a very slow rate so that the insoluble crystals at the bottum of the reaction flask were not carried over into the safety flask. After this separation of solvent from crystals was complete the safety flask and the reaction flask were sealed as before and transferred to the dry box.

The crystals remaining in the reaction flask (product III) were dried under vacuum and analyzed by infrared spectroscopy. The liquid in the safety flask was pumped to dryness at 40°C and yielded a crystaline solid (product IV) which was analyzed for boron and chlorine content. An infrared spectrum from this solid was obtained prior to hydrolysis.

Analysis for Boron and Chlorine.

The analysis of hydrolyzed samples included a titrimetric determination of boron and chlorine, as boric and hydrochloric acid, and a gravimetric determination of chlorine as silver chloride[6]. It was assummed that all boron and chlorine would form boric and hydrochloric acid upon hydrolysis. Titration of aliquots of hydrolyzed samples with sodium hydroxide, using phenylpthalein as indicator, gave first end points corresponding to the neutralization of hydrochloric acid. Upon the addition of mannitol[7] a second end point was obtained for each sample as boric acid was neutralized.

Hydrolysis of most samples was accomplished by adding about one gram of solid sample to several milliliters of water and then diluting to a specific volume. When this procedure was attempted with product IV a violent, exothermic, reaction took place. Dense fumes were given off and an odor similar to that obtained in the hydrolysis of BCl_3 was noted. Hydrolysis of product IV for quantitative analysis was accomplished by vacuum distilling water onto the solid sample at dry ice/acetone temperatures.

Infrared spectra were obtained through the use of mulls, with Nujol (sodium dried) and hexachlorobutadiene (calcium chloride dried) as mulling agents. The mulls were made up in the dry box, and placed between sodium chloride plates. Before the plates were taken from the glove box the crack between the plates was sealed with stopcock grease to prevent hydrolysis of the sample by moisture in the air.

RESULTS

All products collected were of similar appearance. Each was a pale yellow crystaline solid. Hydrolysis of each product, except IV, was without violence. Product IV was stable to vacuum at 40°C for several hours.

Results of Boron/Chlorine Analysis, in Duplicate.

Sample	Boron(meq/g)	Chlorine(meq/g) titrimetric	Chlorine(meq/g) gravimetric	B:Cl ratio
product II	6.80	7.58	10.0	1:1.1 to 1:10*
	5.36	6.08	10.7	
product IV	10.9	9.28	9.47	1.17:1
	11.1	9.11	9.50	1.22:1
$(-BCl-NOMe-)_3$				1:1
$Cl_3B{:}NH_2OMe$				1:3

* Conflicting values for chlorine (titrimetric versus gravimetric) result in a B:Cl ratio ranging from 1:1.1 to 1:10.

DISCUSSION

Product I, from the chlorobenzene system, was a small yield of crystals. The spectrum of product I suggests a mixture including triethylamine hydrochloride and little or no borazine. Peaks in the 2400-2900 cm^{-1} are similar to those found in the literature for Et_3NHCl.

In the second reaction, shortly after the flow of BCl_3 was started, a clean white crystaline material appeared in the lower part of the condenser. The area in which these crystals formed suggests either a reaction between BCl_3 and the solvent vapors or contamination by water. If water entered the system, BCl_3 could be hydrolyzed to boric acid or the $MeONH_3CL$ could be hydrolyzed to give $MeONH_2$ which could then be carried by the refluxing to the lower condenser area, resulting in the formation of the $Cl_3B{:}NH_2OMe$ adduct. The crystals washed down into the pot as the reaction continued and no similar appearing crystals were ever isolated.

The third reaction was intended for the collection of the white crystals noted in the second reaction. Unfortunately no such crystals were formed. For this reason, some source of contamination, probably water, is suspected as the cause of the crystals formed in the second reaction. The crystals collected from the reaction flask after the third reaction (product III) is beleived to be the same compound as product II. This belief is based of infrared spectral peaks at 2955, 1437, 1401, and 1256 cm^{-1} as compared with peaks at 2954, 1430, 1400, and 1252 cm^{-1}. Product IV, obtained from the solvent after the third reaction is believed to be B-trichloro-N-trimethoxyborazine. The

infrared spectrum of product IV will be discussed shortly.

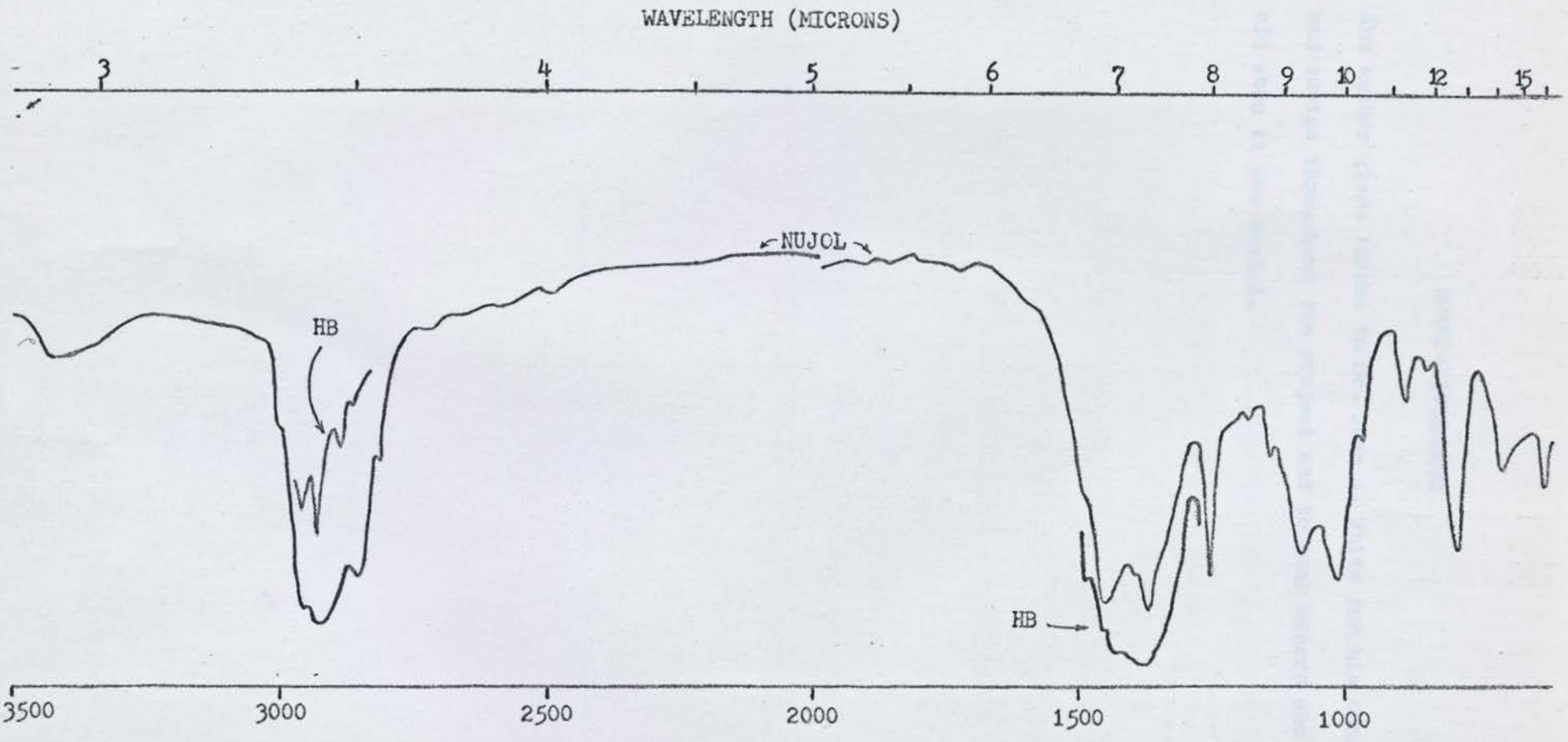
Of the two reaction conditions used, the one involving the chlorobenzene/ chloroform mixture was found to give a much cleaner reaction. The solid found when the solvent of the third reaction was pumped to dryness had no tar-like character and definitely included a compound not previously isolated. All previous reaction products hydrolyzed with no visible signs of reaction other than that they dissolved in water, whereas product IV hydrolyzed with considerable violence. The ratio of boron to chlorine in product IV being 1.2:1 suggests either the B-trichloro-N-trimethoxyborazine, with some loss of chlorine during hydrolysis, or some unknown compound having a boron to chlorine ratio closer to 1.2:1. Traces of $MeONH_3Cl$ or of the $Cl_3B{:}NH_2OMe$ adduct would result in a boron to chlorine ratio of less than 1:1 and therefore may be disregarded. Since the crystals are stable to vacuum at 40°C, no unreacted BCl_3 or chlorinated solvent could be present. Nor would the presence of BCl_3 or chlorinated solvent explain the high value of the boron to chlorine ratio.

Konig reported that spectra obtained from reaction products of methoxyamine hydrochloride and boron trichloride, as obtained with Nujol mulls, were poorly defined. The spectra obtained with mulls made from the reaction products of all three reactions were more useful than those prepared by Konig. Future work should result in much better purities of products and therefore better spectra.

Literature values[9] for B-N streching frequencies in borazine rings are given as about 1400 cm^{-1}. Spectrum of all products show

some absorption in the region arround 1400 cm^{-1}. Of the four products, product IV shows the greatest absorption in this region, having a broad peak from 1300 to 1500 cm^{-1}. Additional spectral evidence for the formation of B-trichloro-N-trimethoxyborazine is the presence of about six peaks which can not be found in spectra of starting materials or of other products.

It would be very useful to repeat the third reaction and more carefully purify the soluble product. Analysis of boron and chlorine content should be done only after a very careful hydrolysis, either in some form of bomb or in a vacuum line, has been carried out.



Infrared Spectrum of Product IV

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